

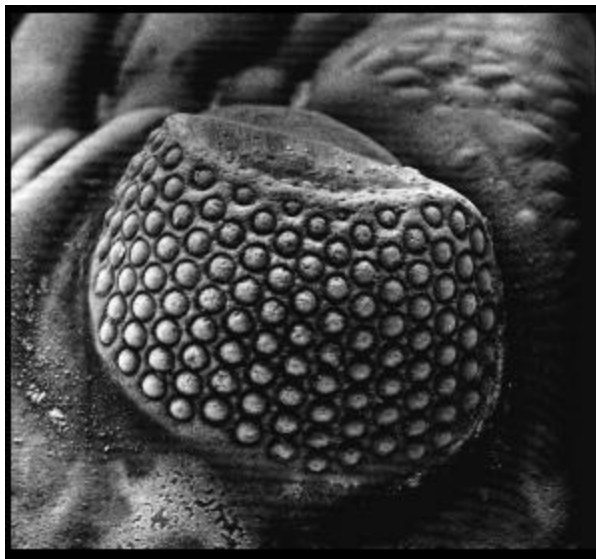
SCIENCE FOCUS: Biogenic Carbonates

An Enlightened View of Calcite in the Ocean with MODIS

College students in an introductory class on mineralogy are very likely to encounter a specimen of a clear, transparent crystal that goes by the name of "Iceland spar" calcite. One of the most obvious properties of this mineral specimen is the visual property of double refraction: viewing something through the crystal provides two images, as shown below.



The visual clarity of calcite might make it a great material for lenses, (if that minor double image problem could be overcome). Trilobites, the ubiquitous organisms that swam in Earth's primordial seas, actually used calcite in the lenses of their multiple eyes. A close-up of the eye of *Phacops* appears below.



Microphotograph of the multiple eye of the trilobite *Phacops*, showing the calcite lenses in the eye.

The chemical formula for calcite is CaCO_3 , or calcium carbonate. CaCO_3 is an important component of Earth's carbon system, primarily because oceanic phytoplankton and zooplankton form shells (also called tests) and skeletons out of this material. One of the most familiar forms of CaCO_3 in the marine realm is the hard skeletons of coral, which form coral reefs and the tropical ring-shaped coral islands called atolls. Beautiful Penrhyn Atoll in the Cook Islands (below) was photographed from the Space Shuttle.



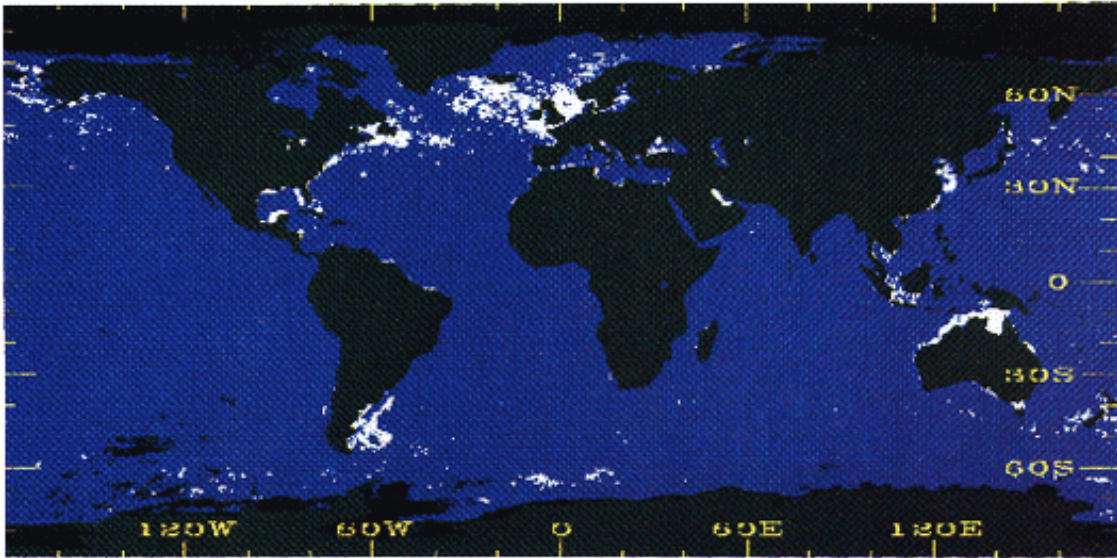
Penrhyn Atoll, Cook Islands

Two major types of phytoplankton, coccolithophorids and foraminifera, create shells made out of calcite. Surprisingly, two types of zooplankton, pteropods and heteropods, form shells made out of aragonite, which is also CaCO_3 but has a different mineral structure. One of the primary questions regarding these organisms is how much CaCO_3 they make, globally, every year.

This question is an important part of the oceanic and global carbon cycle, and it is difficult to reliably estimate. Remote sensing with instruments such as the Coastal Zone Color Scanner (CZCS) and the Sea-viewing Wide Field-of-view Sensor (SeaWiFS) has provided remarkable views of vast blue-white blooms of coccolithophores, but actually quantifying how much CaCO_3 is in those blooms is considerably more difficult.

A quick definition of terms: a coccolithophorid is a particular form of phytoplankton that forms disks of CaCO_3 called coccoliths. The organisms form spherical shells ("coccospheres") out of the coccoliths. Coccolithophorids are microscopic.

A few years before SeaWiFS was launched, Dr. Christopher Brown (now with the National Oceanic and Atmospheric Administration) and Dr. James Yoder of the University of Rhode Island (now with the National Science Foundation) used CZCS data to map the occurrence of coccolithophorid blooms in the world ocean. Click on the map to learn more about monitoring of coccolithophorid blooms, and to see a large micro-photograph of the most common coccolithophorid in the ocean, *Emiliana huxleyi*.



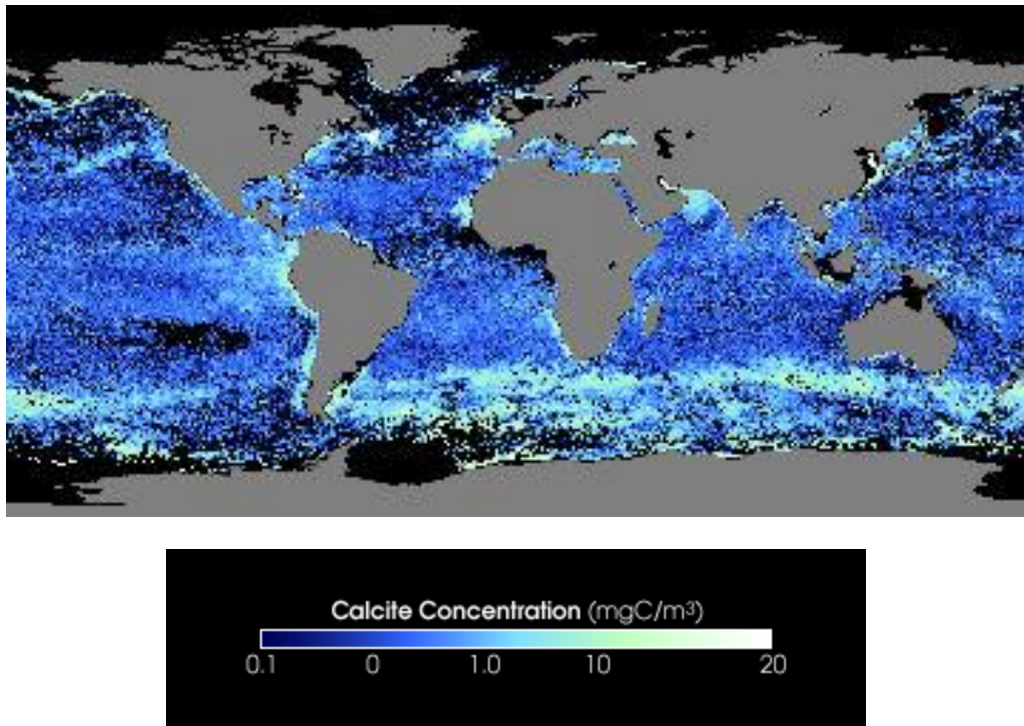
Global map of coccolithophorid bloom occurrence based on CZCS data.

One area in which these blooms frequently occur is in the southern Atlantic Ocean, near the coast of Argentina and the Falkland Islands. A previous *Science Focus!* article, “More Than Meets The Eye”, demonstrated how SeaWiFS data can be used to diagnose the presence of coccolithophorid blooms in SeaWiFS data for an image acquired by SeaWiFS over this oceanic region. In fact, Dr. Brown developed the algorithm that the SeaWiFS Project uses to detect coccolithophorid blooms and “flag” them as areas where the reflective properties of these organisms will lead to erroneous calculation of chlorophyll concentration.

Blooms of coccolithophorids, particularly the widespread *Emiliana huxleyi*, are easily recognized and detected due to their optical characteristics, which give the water a milky turquoise color. The *Science Focus!* article “The Bering Sea: Seasons and Cycles of Change”, has some SeaWiFS images of large coccolithophore blooms in the Bering Sea. Since these blooms can be observed so readily, the next logical research step is to attempt to determine how much calcite they are producing: i.e., to quantify the concentration of the coccolithophores and their coccoliths in the ocean.

And that's where the Moderate Resolution Imaging Spectroradiometer (MODIS) comes into play. Two members of the MODIS Ocean science team, Dr. William "Barney" Balch of the Bigelow Laboratory for Ocean Sciences in Maine and Dr. Howard Gordon of the University of Miami, developed an algorithm that uses MODIS data to quantify the amount of coccolithophorid calcite in these blooms. The algorithm relies on Dr. Gordon's semi-analytical model of water-leaving radiances and Dr. Balch's ongoing research into the optical properties of coccolithophorids and coccolithophorid blooms.

Ever since the MODIS-Terra instrument began acquiring data, and especially following the initiation of observations by MODIS-Aqua, this algorithm has been applied to the global quantification of calcite in the oceans. A small image of the MODIS calcite concentration product for March 2003 is shown below. Some coccolithophore blooms occurring with the early North Atlantic spring bloom can be seen near the coasts of England and France.

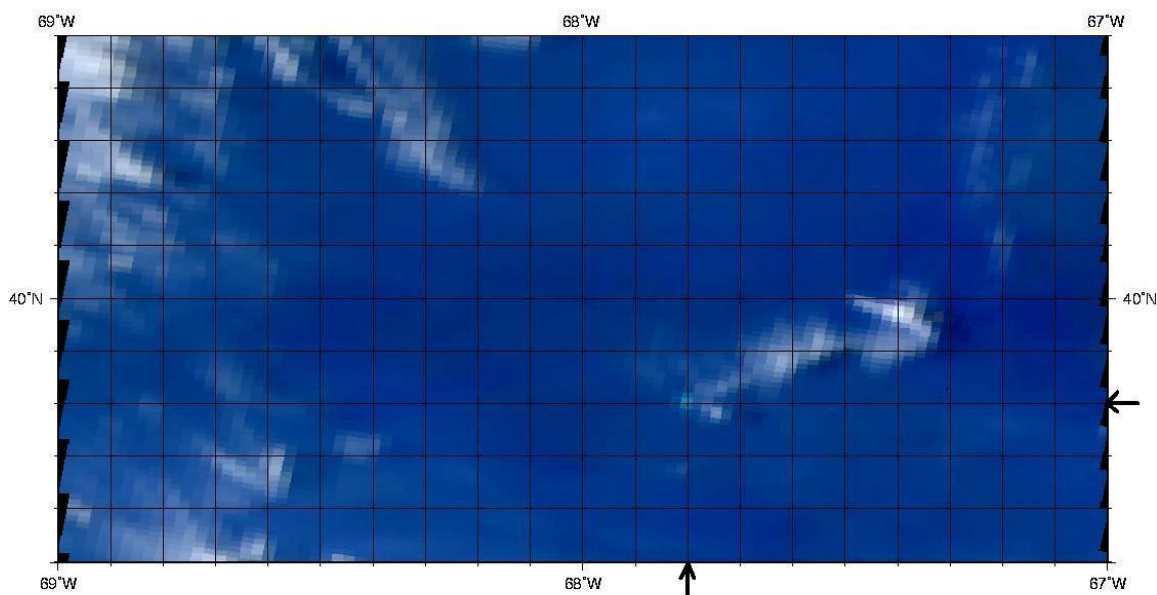


Global map of MODIS coccolithophore calcite product for March 2003, and color scale.

The researchers who developed the calcite concentration algorithm devised two ways to check its accuracy. One way was to sample the recurring *E. huxleyi* blooms in the Gulf of Maine and compare that data to the results calculated by the algorithm. However, it took a few years for nature to cooperate and provide coccolithophore blooms in the Gulf of Maine following the launch of MODIS-Terra in 1998. So the researchers initially went to their "Plan B" to test the algorithm—they dispersed 13 tons of coccolith chalk in the ocean to make an offshore micro-patch of suspended calcite with the same reflectance as naturally occurring blooms (which contain hundreds of thousands of tons of coccolith calcite). The name of this experiment was "Chalk-Ex".



Researchers put tons of chalk, composed of fossil coccoliths, into the ocean for "Chalk-Ex".



SeaWiFS True Color image of the great chalk patch at 39.8 degrees N and 67.8 degrees W acquired on 6 August 2000 at the NASA/Goddard Space Flight Center receiving station.

This image shows what the first "Chalk-Ex" looked like from the viewpoint of SeaWiFS. In this image, only 2 bluish-white pixels (indicated by the arrows) are the actual chalk patch; the rest of the white area is cloud.

Since then, the Gulf of Maine has come through with some nice blooms that could be used to test the accuracy of the algorithm. The MODIS image of the Gulf of Maine shown below was acquired on June 11, 2002. Cape Cod is in the lower left corner of the image, and Nova Scotia at upper right.



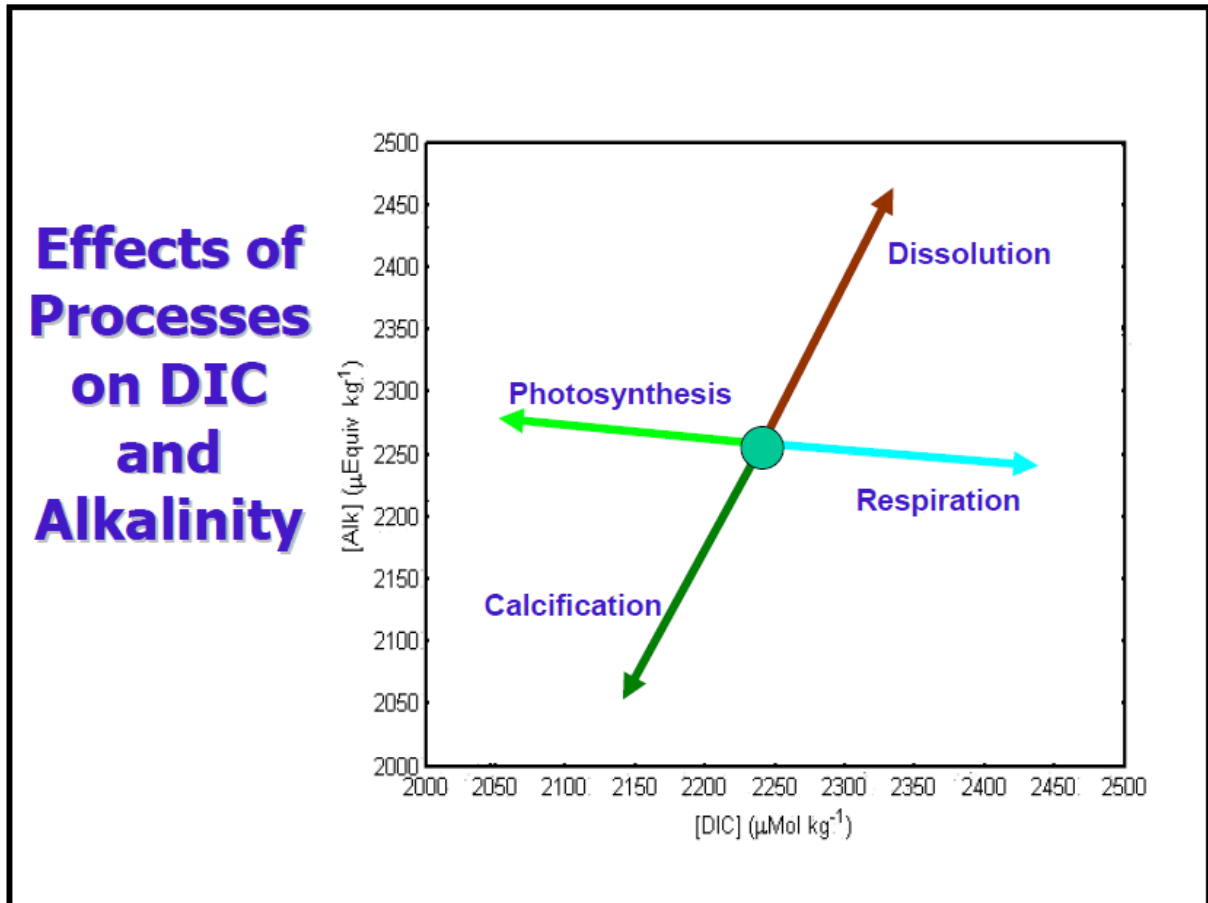
MODIS image of a coccolithophorid bloom in the Gulf of Maine, June 11, 2002. Nova Scotia is the land mass at the upper right of the image, and Cape Cod is clearly visible at lower left.

Now, it's still possible for the algorithm to provide results for conditions that are optically similar to coccolithophore blooms, which is why further analysis of the data is still required. The algorithm shows significant concentrations of coccolithophore calcite in the Southern Ocean, where diatoms made out of silica would be expected to be the dominant organisms. Other conditions, such as suspended sediments near the coast, and even the strange eruptions of hydrogen sulfide gas off the coast of South Africa and Namibia, might also be similar enough to be misidentified as coccolithophore blooms.

Even though the algorithm still needs to be "tweaked" (as of 2003), it represents another great step forward in understanding the oceanic carbon cycle. The reason that calcite and CaCO_3 in general are important is due to the fact that both their formation and dissolution involve carbon and carbon dioxide (CO_2).

Calcite, Carbon, and Carbon Dioxide in the Global Ocean

It would take a few book chapters to go into the details of the chemistry of carbon and carbon dioxide system in seawater, so we'll only discuss the relevant parts of the system.



When marine organisms form CaCO_3 , the biological process of "calcification", CO_2 is produced. However, this process is just one part of the ocean carbon cycle. In the above diagram, "DIC" stands for "Dissolved Inorganic Carbon".

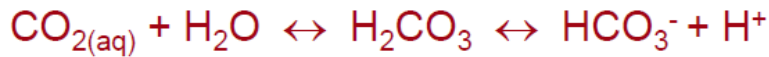
In the open ocean, the organic matter that composes organisms is continuously decomposed by bacteria after the organisms perish. This process, known as respiration, converts the organic carbon into inorganic carbon, which is somewhat confusingly called "mineralization".

Equations for CO₂ Speciation

The equilibrium of gaseous and aqueous CO₂:



Subsequent hydration and dissociation reactions:



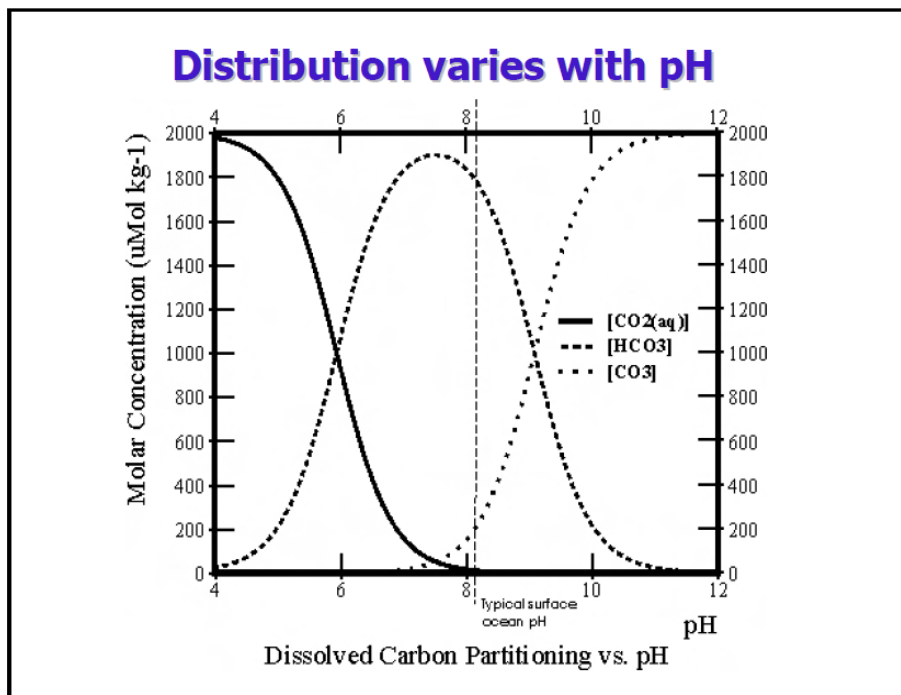
$$K_1^* = \frac{\{H^+\}[\text{HCO}_3^-]}{[\text{CO}_2]}$$



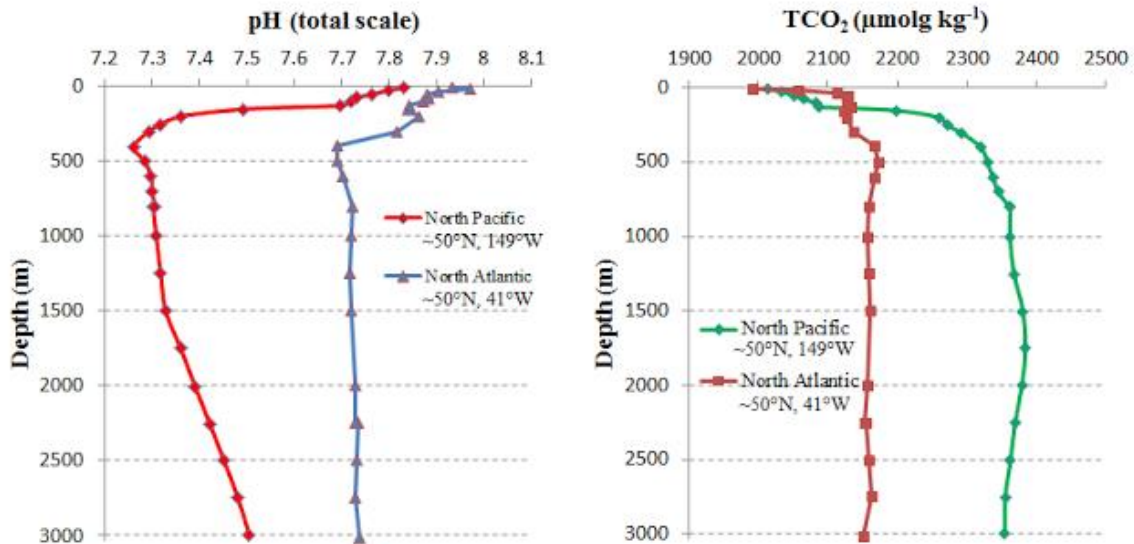
$$K_2^* = \frac{\{H^+\}[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

Asterisk (*) indicates a "stoichiometric" constant

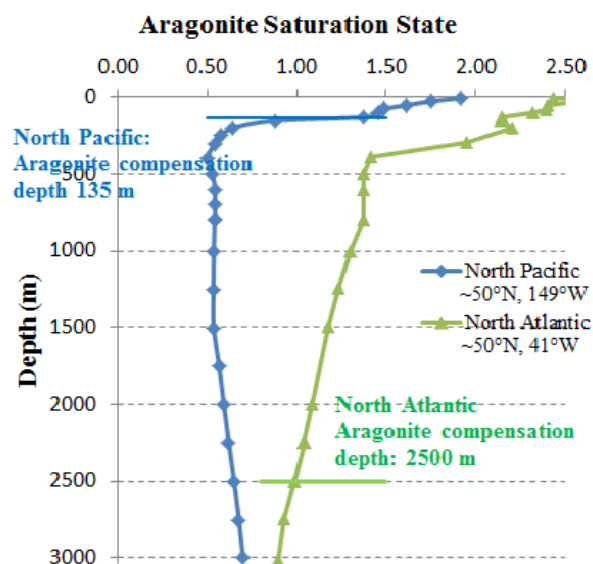
The two major dissolved forms of inorganic carbon in the oceans are bicarbonate ion, HCO₃⁻, and carbonate ion, CO₃²⁻, as shown here. The concentrations vary with pH.



The combined effect of these processes is to increase the quantities total carbon dioxide, TCO_2 , and seawater's **total alkalinity**. The net effect of these processes is to decrease the concentration of CO_3^{2-} in the deep ocean as the water masses age, which means that the water becomes progressively more corrosive to CaCO_3 , i.e., the dissolution of CaCO_3 is increasingly favored. These processes also will lower the pH of seawater.



Because the oceans generally circulate from the north Atlantic Ocean to the north Pacific Ocean, as the water moves it becomes progressively more corrosive to CaCO_3 . The distribution of carbonate sediments composed of coccoliths and foraminiferal CaCO_3 is directly influenced by this process; the sediments are found in much deeper waters in the Atlantic Ocean compared to the Pacific Ocean. That effect is shown in this diagram of the different aragonite saturation states in the Atlantic and Pacific Oceans (diagrams courtesy Aleck Wang).



The reason that these processes are important is that the increasing levels of atmospheric CO_2 will eventually be absorbed by the oceans, and they will slowly change the chemistry of seawater with respect to CaCO_3 . The dissolution of CaCO_3 will actually neutralize (in several thousand years) the CO_2 in the atmosphere. But in the short term, increasing concentrations of CO_2 actually inhibit the ability of organisms to form CO_2 . Thus, the full effects of the interaction of the biology and chemistry in the oceans and atmosphere are still very hard to determine. Getting a better estimate of how much calcite is being produced by myriads of coccolithophorids in the world's oceans is one vital element in increasing our understanding of how the system works, and allowing improved predictions of what might happen in the future.

Links

[Emiliana huxleyi Home Page](#)

[Coccolithophorids](#)

[Distribution of coccolithophorids and coccoliths in surface ocean off northeastern Taiwan](#) (features micro-photographs of many different species)

[Ocean Biogeochemistry: Calcification and \$\text{CO}_2\$](#) (published in *Nature*; subscription may be required)